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COMPOSITION OF A VOLATILE FRACTION OF APPLES

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Our knowledge of the identity of the odorous constituents of apples has not increased appreciably since 1920. In that year Power and Chesnut (1920) reported that the odorous constituents of several varieties of apples consisted essentially of the amyl esters of formic, acetic, and caproic acids, with a trace of the caprylate and a "considerable proportion" of acetaldehyde. Traces of methanol, ethanol, and possibly some free formic, acetic, and caproic acids also were found. Later Power and Chesnut (1922) reported the occurrence of geraniol in McIntosh apples. Ethylene was recognized by Gane (1934) as a constituent of apple emanation. Walls (1942) described the results of chemical examination of a small amount of an odorous oil obtained by adsorbing the volatiles from whole apples on calcium chloride. After hydrolysis, he obtained a dinitrobenzoate, which he tentatively identified as an amyl derivative, and an acidic fraction, in which he obtained color tests for formic and acetic acids.

Interest in the aroma constituents of apples has been revived by the development by Milleville and Eskew (1944) of a process for the recovery from apple juice of the entire volatile odorous fraction in a concentration of about 150 times that in the original juice. This product, termed "apple essence," or "volatile apple concentrate," has a fine, fragrant apple odor. Because information on apple volatiles is relatively scanty, and also because preliminary examination of the new product gave results differing widely from those of Power and Chesnut, a systematic chemical examination was carried out on the volatile apple concentrate.

Results are summarized (Table 1). These data, calculated from refractive indices, saponification equivalents, and amounts of derivatives isolated, represent a rough approximation of the composition of apple volatiles.

The first column gives the identities of the compounds; the second shows the calculated amount of each compound in the original 10.100 kg. of 150-fold volatile apple concentrate, corresponding to the 92.2 g. of apple oil distilled.

The data (Column 3, Table 1) may be converted to the original apple juice basis by dividing by 150. Since no effort was made to extract all the juice from the original apples, or to recover the volatiles from the press cake, calculation of results on the original apple basis would be somewhat misleading. It may be of interest to point out that even assuming all the odorous material from the apples to be in the juice, a concentration in the

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original apple of 0.0035 per cent is obtained. It is also noteworthy that, contrary to results of Power and Chesnut, no amyl esters were identified.

Power and Chesnut (1920) reported their yields of apple oil, from Ben Davis and a crabapple, to be 0.0007 and 0.0013 per cent, respectively. Later (1922), they reported a yield of 0.00027 per cent for McIntosh apples. (The oil was obtained from the peels, which they stated represented 12.5 per cent of the weight of the fruit.) They also described an experiment in which McIntosh apples of the same lot were peeled, quartered, and cored, and the pulp subjected to their recovery procedure. In this case they obtained a yield of 0.00123 per cent on "weight of material employed." However, they then state, "It was evident from this result that the odorous constituents of the fruit are contained most largely in the outer portion or

TABLE 1

Estimated Composition of Apple Volatiles

Component	Amount from 10,100 g. essence	Conc. in 150-fold essence
	g.	*p.p.m.*
Total	76.46	7,560
Acetaldehyde	2.70	260
Acetone	0.08	8
Caproaldehyde	0.97	90
2-Hexenal	0.64	64
Furfural	0.01	1
Methanol	2.00	200
Ethyl alcohol	54.40	5,380
Propyl alcohol	0.76	75
2-Propanol	0.23	23
Butyl alcohol	7.90	780
Isobutyl alcohol	0.20	20
2-Methylbutanol	2.80	270
Hexyl alcohol	2.40	240
Ethyl butrate	0.70	70
Ethyl caproate	0.41	40
Other ester components: Alcohols: Methyl, ethyl, 2-propyl, and butyl. Acids: Formic, acetic, propionic, butyric, and caproic	0.26	26

rind." Calculation shows, however, that (even assuming a one-third loss in weight in coring the apples) the pulp from a given batch of apples would yield 1.82 g. of oil, while the peel would yield only 0.698 g. On the basis of Power and Chesnut's data, the odorous constituents are more concentrated in the outer portion, but because the pulp is the greater proportion of the apple, there is more odorous material in the pulp.

The volatile apple concentrate studied in the present work, being prepared from the juice, is probably more representative of the pulp than of the skin. In pressing the apples, a hammer mill was used to break the fruit, but the particles of skin were not finely divided. The apples were pressed cold, so it is possible that relatively little material from the skin was included in the juice. This may account in part for the wide difference in the composition of apple odorous material reported here, and that reported by Power and Chesnut.

EXPERIMENTAL PROCEDURE

Material: Apples that had been in cold storage for about two months, were sorted to eliminate unsound fruit and washed before pressing. The 10.501 kg. of essence used for this study were obtained from 1,145 kg. of McIntosh and 1,209 kg. of Stayman Winesap apples, by use of the pilot-plant recovery unit previously described by Milleville and Eskew (1944). The 150-fold concentrate was kept cold until used.

Preliminary Concentration: The essence was fractionally distilled at atmospheric pressure in three batches through a total reflux, partial take-off column.[2] During distillation, ice water was circulated through the condenser, and a solid carbon dioxide trap kept on the vent. The receiver was jacketed with ice water. Typical data are shown (Table 2).

TABLE 2

Preliminary Distillation of Volatile Apple Concentrate [1]

Fraction No.	Boiling range	Weight	Phases
	°C.	g.	
1	30-89	39.24	One
2	89-92	33.38	Two
3	92-95	47.76	Two
4	95-97	53.80	Two
5	97-98	55.44	Two
6	98-99.5	35.15	Two

[1] Charge, 4,039 g. Distillation was continued until distillate was water only.

The corresponding fractions from the three distillations were combined and salted out by saturation with anhydrous potassium carbonate.

All material thus obtained was combined to yield 95.8 g. (0.912 per cent of original concentrate) of a light-yellow oil. A small amount (0.28 milliequivalent) of volatile acid was recovered from the potassium carbonate solution.

Properties of Apple Oil: The material had a strong fragrance, not especially characteristic of apples, which on suitable dilution closely resembled the original essence. Qualitative tests for nitrogen, sulfur, and halogen were all negative. It gave a strong Schiff's test and had a saponification equivalent of 1520; $d_{24} = 0.823$; $[\alpha]_{D}^{25} = -0.20° \pm 0.01°$ (homogeneous); $n_{D}^{25} = 1.3755$.

Fractionation of Apple Oil: A Stedman-type column, 17-mm. I. D. with an 80-cm. section packed with 95 stainless steel wire screen cells, as described by John and Rehberg (1949), was used. Ice water was circulated in the condenser, and a solid carbon dioxide trap kept on the vent during distillation. Ninety-two-and-two-tenths g. of the "anhydrous" oil

[2] The column, 2.5-cm. I. D., had a 122-cm. section packed with 4-mm. glass helices. It has a HETP = 3.3 cm. at 480 ml./hr. boil-up with a heptane-methylcyclohexane mixture.

were used (equivalent to 10.100 kg. original concentrate), and nitrogen was passed in slowly during distillation. A total of 16 fractions was obtained over the range from 21°/750 mm. to 170°/3 mm. Fraction 17 consisted of the material remaining on the column after distillation; it was removed by washing the column with acetone. The data are shown (Table 3). Saponification equivalents, calculated as if the entire fraction were an ester, are also shown in the table.

TABLE 3

Fractional Distillation of Apple Oil[1]

Fraction No.	Boiling range	Pressure	Weight	n_D^{20}	Saponification equivalent
	°C.	mm.	g.		
1	21-23	750	1.67	....	....
1a	23-35	750	0.01	....	....
2	35-66	750	1.30	1.3665	750
3	66-75	750	1.84	1.3485	1,550
4	75-78.5	750	20.42	1.3620	10,520
5	78.5-79.5	750	34.45	1.3635	11,900
6	79.5-80.5	750	1.50	1.3672	1,760
7	80.5-85	750	1.77	1.3760	580
8	85-89	750	2.42	1.3938[2]	........[3]
9	89-92	750	1.52	1.4060[2]	....
10	92-93	750	12.41	1.3961[2]	....
11	56-84	150	1.88	1.4060[2]	....
12	84-90	150	1.44	1.4080	1,940
13	90-100	150	0.98	1.4104	2,460
14	100-110	150	0.73	1.4151	1,570
15	61-62	14	2.03	1.4202	3,060
16	63	14			
	to 150	3.0	0.31	1.4270	1,200
17[4]	170	3.0	1.93	1.4570	491
Pot residue	....	......	1.2	....	Tar

[1] Reflux ratios: Fraction 1, 7:1; 2-13, 20:1; 13-16, 5:1. Boilup, 180 ml./hr. [2] n_D^{20} for upper layer. These fractions consisted of two phases. [3] See Table 4. [4] This fraction is the residue obtained from the column only.

Fractions 8 to 11 consisted of two phases, showing initial dehydration was incomplete. Each of these fractions was saturated with potassium carbonate, and the upper layer removed. Data on these upper layers are shown (Table 4).

CHEMICAL EXAMINATION OF FRACTIONS

Methods: Each of the fractions (Tables 3 and 4) was treated by appropriate methods for identification of carbonyl compounds, alcohols, and esters. General procedures followed are outlined below:

Carbonyl Compounds: The 2,4-dinitrophenylhydrazones were prepared as described by Allen (1930). The products (or the entire reaction mixture, transferred to ether and washed alcohol-free if no solid derivative was obtained) were subjected to chromatographic adsorption on a bentonite column by the method of White (1948). By this procedure, crystalline derivatives were obtained, even when the quantity present was too small to crystallize from the reaction mixture. Derivatives were identified by mixed melting points and by analysis.

Alcohols: Portions of the fractions were treated with a 10 per cent excess of 3,5-dinitrobenzoyl chloride, in the presence of only sufficient pyridine to combine with the HCl evolved. They were boiled one minute, transferred to a distillation flask with water, and distilled until the distillate was no longer fragrant. The distillate was reserved for identification of esters, the residue cooled and filtered. The solid was treated with an excess of two per cent sodium carbonate solution, filtered, and the insoluble material crystallized from aqueous ethanol. The dinitrobenzoates were then subjected to chromatographic adsorption on silicic acid-rhodamine 6G by the method of White and Dryden (1948), and if necessary the eluted fractions fractionally crystallized. They were identified by mixed melting points and elementary analysis.

TABLE 4

Salting Out of Diphasic Distillation Fractions

Fraction No.	Oil obtained	n_D^{20}	Saponification equivalent
	g.		
8	2.02	1.3950	460
9	1.24	1.4061	540
10	7.57	1.3990	4,530
11	0.94	1.4110	770

Esters: The aqueous distillate from the alcohol procedure contained any esters originally present, together with any alcohols unreacted with the dinitrobenzoyl chloride. It was hydrolyzed by boiling for from five to 10 hours with an equal volume of 20 per cent aqueous sodium hydroxide, and the alcohols distilled off the alkaline solution through an 18-inch Vigreux column. After addition of 0.3 ml. pyridine, the distillate (from two to 10 ml.) was saturated with anhydrous potassium carbonate and without separation of the phases one ml. of benzene and about 0.5 g. 3,5-dinitrobenzoyl chloride were added. After the reaction had subsided, the reaction mixture was transferred to a separatory funnel with ether and water, washed with water, and evaporated to dryness. The residue was then adsorbed from petroleum ether on silicic acid-rhodamine 6G, for the separation of the alcohol derivatives. By comparison of the compounds found here, with those found as free alcohols, it was usually possible to ascertain which alcohols were from esters and which were free. With this procedure, it was possible to isolate and identify as little as two mg. of an alkyl dinitrobenzoate, provided it was chromatographically separable. The potassium carbonate procedure outlined above usually gave a yield of about 50 per cent of a derivative, even though the alcohol was in a 0.5 per cent aqueous solution.

The acids from esters were in all cases volatile. They were distilled off the acidified saponification solution, titrated, and subjected to partition chromatography on wet silicic acid by the procedure outlined by Ramsey and Patterson (1945). The fractions (either filtrates or eluates) were titrated, evaporated dry, and when sufficient material was available (at least 0.02 milliequivalent), converted to the anilide. The procedure for this is of interest, in that no special micro equipment was used. The sodium salts were evaporated in a 16-x-150-mm. test tube, 0.15 ml. of thionyl chloride was added with stirring, and after heating to boiling, about five ml. of benzene added and the tube shaken. Then 0.40 ml. of aniline in about three ml. of benzene was added with shaking, the tube boiled 30 seconds, cooled, and transferred with ether (about 25 ml.) and water (about 10 ml.) to a separatory funnel, and washed with five ml. of five per cent sodium hydroxide, five ml. of five per cent hydrochloric acid, and three times with water. The upper layer was then evaporated dry on a steam bath in a current of air. The product was crystallized by dis-

TABLE 5

Alcohols and Carbonyl Compounds Isolated as Derivatives

Fraction No.	Compounds isolated as derivatives
Cold trap	Acetaldehyde
1	Acetaldehyde
2	Acetaldehyde, acetone, methanol
3	Acetaldehyde, acetone, methanol, ethyl alcohol
4	Acetaldehyde, acetone, ethyl alcohol
5	Ethyl alcohol
6	Caproaldehyde, ethyl alcohol
7	Caproaldehyde, ethyl alcohol, 2-propanol
8	Caproaldehyde, 2-hexenal, ethyl alcohol, propyl alcohol, isobutyl alcohol
9	Caproaldehyde, 2-hexenal, ethyl alcohol, propyl alcohol
10	2-Hexenal, butyl alcohol
11	2-Hexenal, butyl alcohol, d-2-methyl-1-butanol
12	2-Hexenal, d-2-methyl-1-butanol
13	2-Hexenal, furfural, d-2-methyl-1-butanol
14	d-2-methyl-1-butanol
15	2-Hexenal, hexyl alcohol
16	Hexyl alcohol
17	Hexyl alcohol

solving it in about three ml. of petroleum ether [b. p. 60 to 67°C.(140 to 153°F.)] and allowing it to evaporate to dryness, either at room temperature or in an ice bath. The crystalline product was identified by melting point and mixed melting point, and by comparison of its X-ray powder diffraction pattern with those published by Matthews and Michell (1946). Only rarely was it necessary to treat the product with activated carbon. The order of washes of the ether solution (alkali, then acid) was the reverse of that generally used and produced a much purer product.

Constituents of the Fractions: Compounds isolated from the various fractions as derivatives are shown (Table 5). Since the same compound was usually found in several adjoining fractions, in most cases only one isolation product was quantitatively analyzed; the rest were identified by melting points and mixed melting points.

CARBONYL COMPOUNDS

Analytical data on the carbonyl compounds isolated from the apple essence are given (Table 6). Of these compounds, acetaldehyde is present in the largest quantity. Also of interest is 2-hexenal, since it has been obtained by steam distillation of the leaves of a large number of plant species. Nye and Spoehr (1943) state that in leaves it is probably an artifact, possibly being formed enzymatically when ruptured leaf cells are exposed to oxygen. Takei, Sakato, Ono, and Kuroiwa (1933 and 1938) hold it in part responsible for the "green" odor of cut grass, and believe that 2-hexenal and the corresponding alcohol are responsible for the aroma of tea. 2-Hexenal DNPH has been reported by Takei *et al.* (1938) to melt at 144°C.(291°F.) and by Tsujimura (1938) at 196°C.(385°F.). Its semicarbazone has been reported by Takei *et al.* (1938) to melt at 173°C.(343°F.); by Delaby and Guillot-Allegre (1933) to melt at 175 to 176°C.(347 to 349°F.); and by Prevost (1944) at 179°C.(354°F.). The boiling point and refractive index are given by Prevost (1944) as $B_{760} = 146°$, $n_D^{17} = 1.4480$; by Delaby and Guillot-Allegre (1933) as B. P. 150°, $n_D^{21} = 1.4470$.

TABLE 6

Volatile Carbonyl Compounds From Apples

Fraction No.	Compound	Dinitrophenylhydrazone MP	Mixed MP	Analyses Calcd.	Analyses Found
		°C.	°C.	pct. N	pct. N
1	Acetaldehyde	156-157	....	24.95	25.05
2	Acetone	123.5-124.5	125-126	23.50	23.27
8	Caproaldehyde	107-108	107-108	20.00	20.46
10, 11	2-Hexenal[1]	146-146.5	146-147	20.12	20.27
13	Furfural	229-231	....	....	....

[1] See text.

For reference purposes, a hexenal was prepared in poor yield by hydrogenation of 2,4-hexadienal[3] at two to three atmospheres' pressure with Raney nickel. The fraction boiling at 145 to 147°C.(293 to 297°F.), $n_D^{25} = 1.4412$), yielded a DNPH melting at 141.5°C.(287°F.); chromatography and recrystallization raised this to 146.5 to 147°C.(295 to 297°F.). *Analysis:* Calc. for $C_{12}H_{14}N_4O_4$: 51.80 per cent C, 5.04 per cent H, and 20.12 per cent N. Found: 51.75 per cent C, 4.79 per cent H, and 20.20 per cent N. The semicarbazone melted at 174°C.(345°F.).

A sample of the fraction of the synthetic preparation, which boiled at 145 to 147°C.(293 to 297°F.), was oxidized with hot chromic acid solution. Volatile acids were separated by partition chromatography; butyric acid predominated. Its anilide was prepared, and its melting point was 92.5 to 94° C.(199 to 201° F.). When mixed with butyranilide, the melting point was 92.5 to 94°C. This located the double bond in the α,β-position in the aldehyde.

[3] The 2,4-hexadienal was kindly supplied by Carbide and Carbon Chemicals Company.

The melting point of a mixture of the DNPH from apples with the synthetic hexenal DNPH was 146 to 147°C.; hence the apple aldehyde was 2-hexenal.

ALCOHOLS

Data on identification of the free alcohols from apple volatiles are summarized (Table 7). Assuming all the optical rotation of the original oil to be due to d-2-methylbutanol, it may be calculated that 3.1 g. were present in the sample examined. The corresponding value (from Table 1) by isolation is 2.8 g.

TABLE 7

Identification of Volatile Alcohols From Apples

Fraction No.	Compound	3,5-dinitrobenzoate					
		MP	Mixed MP	Analyses			
				Calculated		Found	
		°C.	°C.	pct. C	pct. H	pct. C	pct. H
2	Methanol	106-107	107-108	42.50	2.67	42.47	2.74
5	Ethanol	91-92	92	45.00	3.33	45.00	3.58
7	2-propanol	98.5-103	111	47.10	3.94	46.93	3.88
8	Isobutanol	77-79	79-83	10.45[3]		10.62[3]	
9	d-2-methylbutanol	81.5-82.5[1]	82-84[2]	51.10	4.90	51.09	5.04
10	Butanol	61.5-63	61.5-63	49.25	4.48	49.36	4.67
16	Hexanol	57-58	57-58	52.75	5.40	52.76	5.30

[1] Derivative had $[\alpha]_D^{25} = +4.4°$ (4.8 per cent in acetone). [2] See White and Ratchford (1949).
[3] Per cent nitrogen.

ESTERS

No esters, as such, were isolated. Four ester alcohols and five acids from esters were identified. Since, after saponification, most distillation fractions examined for esters contained at least two alcohols and five acids, the question of which alcohol and which acid formed the ester is left unanswered.

The procedure outlined under "Esters" was applied to all fractions with saponification equivalents of about 2,000 or below, provided material was available. Obviously, where the esters were mixed with much larger quantities of various alcohols, there was occasionally doubt as to which alcohol was from the hydrolyzed ester and which occurred free. Semi-quantitative data on proportions of the various alcohols before and after saponification, obtained from the weights of derivatives, were used when necessary to identify the ester alcohol. Amounts of volatile acids as determined by titration after distillation were in agreement with amounts of total acids as calculated from the determination of saponification equivalent; thus all acids produced from the esters were volatile.

Results obtained are summarized (Tables 8 and 9). Ethyl esters predominated. Data are included (Table 9) which show the amount of each acid recovered from the partition column as per cent of the original sample taken for analysis. This serves to indicate the relative occurrence of the various esters.

Thus, it is evident that although positive identifications of several alcohol and acid components were made, actually no esters were positively and unequivocally identified. The ester alcohols present were methanol, ethyl,

TABLE 8

Characterization of Alcohol Part of Esters as Dinitrobenzoates[1]

Fraction No.	Compound	MP	Mixed MP
		°C.	°C.
3	Methyl	103-104.5	103-105
	Ethyl	90-92	91.5-93
8	Ethyl	92-92.5	92-93
	2-propyl	83-90	109-116
9	Ethyl	91-92	91.5-92.5
12	Ethyl	89-91	90-93
	Butyl	60-62	60-62.5
14	Ethyl	88-92	....
	Butyl	54-64	....
17	Ethyl	91.5-92	91.5-92.5
	Butyl	51-53	51-64

[1] Small quantities generally obtained precluded microanalyses.

TABLE 9

Characterization of Acid Parts of Esters as Anilides

Fraction No.	Acid	Amount in fraction	Identification Method		
			MP	Mix MP	Other
		pct.	°C.	°C.	
3	Acetic	0.36	....	....	Position[1]
	Propionic	0.45	....	....	X ray[2]
8	Formic	0.12	49	....	....
	Acetic or propionic	(0.4)	102	....	....
	Butyric	6.7	93.5-94.0	94-94.5	X-ray
	Caproic	1.9	95.5-96.0	....	X-ray
9	Formic	0.67	....	....	Position
	Possibly acetic	0.15	....	....	Position
	Possibly propionic	0.21	....	....	Position
	Butyric	6.4	93	94	X ray
	Mixture	1.5	....	....	X ray
	Caproic	4.1	94	94.5	X-ray
12	Formic	0.10	....	....	Position
	Acetic	0.41	....	....	X ray[3]
	Caproic	1.8	....	....	X-ray
14	Formic	0.19	....	....	Position
	Acetic	0.49	112-115	112-114	....
	Propionic	0.15	....	....	Position
	Butyric	0.69	89-90	90.5-93	....
17	Acetic	0.73	....	....	X ray
	Propionic	0.45	....	....	X ray
	Caproic	2.4	....	....	X-ray

[1] "Position" refers to probable identity of compound by its position on the partition chromatographic column, in relation to identified acids. [2] Refers to identification by x-ray powder diffraction pattern. [3] Single crystal x-ray diffraction pattern.

2-propyl, and butyl alcohols; the acids from esters included formic, acetic, propionic, butyric, and caproic. Presence of ethyl butyrate and ethyl caproate in one fraction was established (Fraction 9). Ethyl formate, acetate, and propionate were also probably present.

SUMMARY

The chemical composition of the aroma of apples has been investigated. The principal components, together with the relative amounts of each class, are alcohols (92 per cent): methanol, ethyl alcohol, propyl alcohol, 2-propanol, butyl alcohol, isobutyl alcohol, d-2-methyl-1-butanol, and hexyl alcohol; carbonyl compounds (six per cent): acetaldehyde, acetone, caproaldehyde, and 2-hexenal; esters (two per cent): ethyl butyrate and ethyl caproate. Methanol, ethyl alcohol, 2-propanol, butyl alcohol, and formic, acetic, propionic, butyric, and caproic acids were identified as components of other esters. These compounds are present in the original apple juice at a total concentration of approximately 50 parts per million.

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